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Two chromium(II) complexes with amidato-like ligands: a compound with the longest Cr–Cr bond and a mononuclear compound with D_{2d} symmetry

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Abstract

Reactions of chromium(II) with ligands that possess an amidato portion have been investigated, and products of two reactions been structurally characterized by X-ray crystallography. They show very different chemical behavior. The 2.550(4) Å chromium–chromium distance in the dinuclear saccharinate, $Cr_2(C_7H_4NO_3S)_4 \cdot 2THF$ (**1**), is the longest found so far in any chromium(II) dimer. Compound **1** also has the shortest chromium–axial ligand distance, Cr–L_{ax}. The reaction of $Cr_2OAc_4 \cdot 2H_2O$ with lithium diethylbarbiturate yielded the mononuclear complex $Li_2Cr(C_8H_{11}N_2O_3)_4 \cdot 2C_2H_5OH$ (**2**), in which the ligand binds to the metal center in a monodentate fashion and there are only Cr–N bonds, which might be taken as an extreme manifestation of a Jahn–Teller Effect. The anion is further distorted from planarity and the coordination about the chromium atom has S_4 symmetry. The crystallographic data for **1** are: space group C_2/c, $a = 22.467(5)$, $b = 21.458(5)$, $c = 11.640(7)$ Å, $\beta = 112.85(2)°$, $V = 5171(3)$ Å^3, $Z = 4$; and those for **2** are: space group *Fdd2*, $a = 27.036(9)$, $b = 17.154(4)$, $c = 20.777(9)$ Å, $V = 9636(10)$ Å^3, $Z = 8$.

Introduction

The commonest compounds of chromium(II) comprise Jahn–Teller distorted six coordinate complexes, a lesser number of square planar complexes at the limit of the distortion, and a large group of dinuclear compounds with Cr–Cr bonds [1].

Work done in our laboratories on chromium(II) and vanadium(II) saccharinates [2] has provided interesting results. Among these are the formation of some mononuclear compounds with a very high stability toward air, different ways of binding of the saccharinate ion (Sac, **I**) through the oxygen atom of the carbonyl group or the nitrogen atom, and the formation of solid solutions.

In the context of the dinuclear complexes, amidato type ligands, with –N–C–O units, are also of interest because their compounds have been found to possess very short [3] and very long Cr–Cr distances [4].

Among the factors that affect the Cr–Cr bond lengths are the inductive properties of the ligands [5]; thus the pK_a of the parent acid of like ligands is very important [6]. Of similar importance is the nature of axial coordination [1, 7]. In the case of the tetracarboxylato complexes a rough correlation has been established that shows that shorter Cr–L_{ax} distances accompany longer Cr–Cr bonds.

In the present work, saccharinate complexes of chromium(II) were considered because of the great versatility of the ligand in its binding of metal atoms and because the study of a possible dinuclear complex could provide a comparison with the previously characterized compound $Cr_2(oxindolato)_4(oxindole)_2$ [4] that has a very long chromium-to-chromium bond of 2.495(4) Å.

The oxindole (Oxd, **II**) is a much stronger base than the saccharinate anion; also, the latter could provide a sterically more hindered environment at the axial position should a dinuclear compound form.

In the same way, stick and ball models of a possible dimer of the diethylbarbiturate anion (Etbarb, **III**) showed it to be even more restrictive to the accom-

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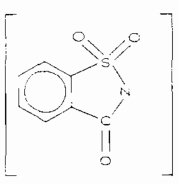
modation of an axial ligand; and so we also decided to look at the product of the reaction of $Cr_2OAc_4 \cdot 2H_2O$ with LiEtbarb.



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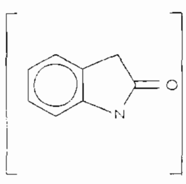
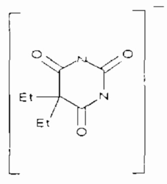


II



III

Experimental

Preparation of compounds

All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques.

$Cr_2(Sac)_4 \cdot 2THF$

To $CrCl_2$ (0.5 g, 4.0 mmol) and 1.01 g (8.1 mmol) sodium pivalate were added 25 ml THF. The green suspension was stirred at room temperature for 8 h until the color changed to reddish brown and was filtered to eliminate sodium chloride; then 18 ml of the filtrate was added to a solution of 1.5 g (4.0 mmol) lithium saccharinate in 40 ml THF cooled to −70 °C and then it was allowed to warm to 5 °C. After a few hours crystals slowly formed. Yield 50%.

The compound without solvent molecules was obtained as follows: 2.0 g (11 mmol) lithium saccharinate and 0.80 g (2 mmol) $Cr_2(OAc)_4 \cdot 2H_2O$ were stirred in 30 ml absolute ethanol for 3 h. A reddish brown precipitate formed. The product was filtered and washed with 3×5 ml absolute ethanol and dried *in vacuo* for 2 h. Yield 72%.

Another way to obtain this compound is by stirring $Cr_2(C_7H_4NO_3S)_2(H_2O)_4 \cdot 2H_2O$ and polar solvents like ethanol, THF or CH_3CN. *Anal.* Calc.: Cr, 12.5; $C_7H_5NO_3S$, 85.5. Found: Cr, 12.0, $C_7H_5NO_3S$, 86.7%.

IR (cm^{-1}): 3400b, 1620s, 1480m, 1380s, 1330s, 1260w, 1170s, 1120s, 930m, 870w, 798m, 750m, 670m.

$Li_2Cr(Etbarb)_4 \cdot 2EtOH$

0.458 g (1.21 mmol) $Cr_2OAc_4 \cdot 2H_2O$ and 1.888 g (9.93 mmol) LiEtbarb were stirred with 35 ml absolute ethanol. The solution changed from red to purple, and after one hour a light blue precipitate was formed. It was filtered and dried *in vacuo*. Yield 53%.

Suitable crystals for X-ray crystallographic studies were obtained by diffusion of the reaction mother liquor with hexane. The compound is air sensitive.

Crystallographic studies

A summary of crystal data and data collection parameters for each compound is given in Table 1. For both samples, X-ray data collection was conducted according to established procedures [8], the commercial package SDP/V V3.0 was used for data reduction, and the program SHELX-76 was used for refinement. For $Cr_2(Sac)_4 \cdot 2THF$, calculations were done on a VAX-11/780 computer, and for $Li_2[Cr(Etbarb)_4] \cdot 2EtOH$ all computations were done on a local area VAX cluster.

For the structure of $Cr_2(Sac)_4 \cdot 2THF$, a crystalline rhombic plate, mounted in a glass capillary tube, was used for all geometrical and intensity data collection. The lattice dimensions, lattice type and Laue group were established by normal-beam oscillation photography. The positions of the two unique chromium atoms were found by direct methods, and the remainder of the non-hydrogen atoms were located and refined in a series of alternating least-squares refinements and difference Fourier maps. The hydrogen atoms on the saccharinate ligands were included at calculated positions, with a common fixed isotropic displacement parameter. A minor disorder of the β-carbon atoms of the axial THF molecules was evident in the large anisotropy of their displacement parameters. The nature of this disorder is well understood in terms of a superposition of two conformers with common oxygen and α-carbon atom positions. We did attempt to resolve the disorder in the β-carbon sites; however, the mean positions of the atomic sites for the two conformers are too close to be treated as separate entities. Accordingly, we refined each unique β-carbon atom as a single site with anisotropic displacement, so that our model would most accurately represent the pattern of electron density represented by the X-ray data. The refinement converged with residuals given in Table 1. Atomic coordinates for $Cr_2(Sac)_4 \cdot 2THF$ are listed in Table 2. For $Li_2[Cr(Etbarb)_4] \cdot 2EtOH$, a crystal was mounted at the end of a glass fiber and placed on the diffractometer in a nitrogen stream at −56 °C. Near the beginning of data collection, the diffractometer failed; and the crystal remained on the goniometer in the nitrogen stream for about ten days while we waited for the arrival of a manufacturer's representative to repair the instrument. After that, data collection from the same crystal was started from the beginning.

Axial photographs were used to confirm the lattice dimensions, lattice type and Laue group. During intensity data collection the intensities of three reflections were re-measured periodically, and showed no significant change over a period of 40.5 h of X-ray exposure. Azimuthal scans of 9 reflections were

TABLE 1. Crystal data for $Cr_2Sac_4 \cdot 2THF$ (**1**) and $Li_2[Cr(Etbarb)_4] \cdot 2EtOH \cdot 0.5EtOH \cdot 0.5H_2O$ (**2**)

	1	**2**
Formula	$Cr_2S_4O_{14}N_4C_{36}H_{32}$	$CrC_{37}H_{60}N_8O_{15}Li_2$
Formula weight	976.9	922.80
Space group	*C*2/*c*	*Fdd*2
Systematic absences	$(hkl),\ h+k \neq 2n$ $(h0l),\ l \neq 2n$	$(hkl),\ h+k,\ h+l,\ k+l \neq 2n$ $(0kl)\ k+l \neq 4n$ $(h0l),\ h+l \neq 4n$
a (Å)	22.467(5)	27.036(9)
b (Å)	21.458(5)	17.154(4)
c (Å)	11.640(7)	20.777(9)
β (°)	112.85(2)	
V (Å^3)	5171(3)	9636(10)
Z	4	8
d_{calc} (g/cm^3)	1.26	1.272
Crystal size (mm)	0.2×0.2×0.1	0.56×0.48×0.22
μ (Mo Kα) (cm^{-1})	6.19	3.223
Data collection instrument	Syntex P$\bar{1}$	Enraf-Nonius Cad-4S
Radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	
Orientation reflections: no.; range (2θ) (°)	15; 10–25	25; 20.5–29.8
Temperature (°C)	5	-56 ± 1
Scan method	ω	ω-scans
Data collection range, 2θ (°)	4–45	4–50
No. unique data, total with $F_0^2 > 3\sigma(F_o^2)$	2720, 1650	2306, 1749
No. parameters refined	311	298
Transmission factors, max., min		obs. 1.00, 0.97
R[a]	0.068	0.0448
R_w[b]	0.070	0.0563
Quality-of-fit indicator[c]	1.866	1.367
Largest shift/e.s.d., final cycle	0.6	0.34
Largest peak (e/Å^3)	0.5	0.38

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

used as the basis of an absorption correction. Following data collection we observed that the crystal decomposed within seconds of its removal from the nitrogen cold stream.

The structure of $Li_2[Cr(Etbarb)_4] \cdot 2EtOH$ was solved by direct methods and developed in alternating difference Fourier maps and least-squares refinements. The amidato hydrogen atoms of the two unique Etbarb ligands were located and refined freely. The hydrogen atoms of the ethyl groups were placed at calculated positions, although most of them had also appeared in a difference Fourier map. The C–H distances were first restrained; then for the final refinement, the ethyl hydrogen atoms were treated as riding on their parent carbon atoms, with one common hydrogen displacement parameter per ethyl group. In the initial restrained refinement it was clear that the three hydrogen atoms attached to C(8) were indeterminate; accordingly, they were omitted from the final refinement. An independent ethanol molecule was located and refined; it is ligated to the unique lithium ion. The hydroxyl hydrogen atom of this ethyl group was also located and refined independently with a weak geometrical restraint ($d = 0.88 \pm 0.05$ Å) placed on the O–H distance.

An area of interstitial electron density comprising four atomic sites, was also located. Two of the sites are related to the other two by a crystallographic two-fold axis. We refined several models for this region, each comprising a different combination of superposed ethanol and water moieties. This involved in most cases, refining sites with mixed carbon and oxygen atom populations. In addition to the relative populations of the two unique sites, we also refined the overall population of the region in alternate cycles. The model refined in the final analysis consisted of equal fractional populations (multiplicity 0.25) of water and ethanol at the site. We do not claim to have arrived at a unique model for this region; nor do we claim that the composition of the crystal remained constant through the long period that it was on the goniometer. The enantiomorph for the structure of $Li_2[Cr(Etbar)_4] \cdot 2EtOH$ was established at the 99% level by a statistical significance test on the weighted least-squares residuals from parallel refinements of both enantiomorphs.

We have computed various stoichiometry-related quantities in Table 1 on the basis of the final model,

TABLE 2. Positional parameters and equivalent isotropic displacement parameters (Å^2) and their e.s.d.s for $Cr_2Sac_4 \cdot 2THF$ (**1**)

Atom	*x*	*y*	*z*	*B* (Å^2)[a]
Cr1	0.5	0.2000(1)	0.25	2.92(9)
Cr2	0.5	0.3189(1)	0.25	2.79(9)
S1	0.6356(2)	0.3621(2)	0.4869(3)	4.0(1)
S20	0.4562(2)	0.1565(2)	0.4822(3)	4.0(1)
O1	0.5911(4)	0.2005(4)	0.3768(7)	3.2(3)
O2	0.6614(5)	0.4014(5)	0.4167(9)	5.7(3)
O3	0.6025(5)	0.3915(5)	0.5544(8)	5.3(3)
O11	0.4591(4)	0.3187(4)	0.3737(7)	3.5(3)
O12	0.4048(6)	0.1159(5)	0.4100(9)	5.9(4)
O13	0.5166(5)	0.1274(5)	0.5537(8)	5.2(3)
O21	0.5	0.4206(6)	0.25	4.8(5)
O31	0.5	0.0987(6)	0.25	4.7(5)
N1	0.5894(5)	0.3068(5)	0.3948(9)	3.4(3)
N11	0.4681(5)	0.2129(5)	0.3945(9)	3.4(3)
C1	0.6161(6)	0.2485(6)	0.429(1)	2.9(4)
C2	0.6780(6)	0.2506(7)	0.541(1)	3.6(4)
C3	0.6941(7)	0.3100(7)	0.584(1)	4.0(4)
C4	0.7487(9)	0.323(1)	0.691(1)	6.0(6)
C5	0.7864(8)	0.273(1)	0.747(2)	6.5(6)
C6	0.7708(8)	0.214(1)	0.706(2)	5.5(6)
C7	0.7154(7)	0.2008(8)	0.600(1)	4.4(5)
C11	0.4543(6)	0.2683(7)	0.428(1)	2.9(3)
C12	0.4323(6)	0.2661(7)	0.532(1)	3.1(4)
C13	0.4322(7)	0.2085(7)	0.575(1)	4.1(4)
C14	0.4145(9)	0.1958(8)	0.673(1)	5.5(6)
C15	0.3989(9)	0.2445(9)	0.728(1)	6.9(7)
C16	0.400(1)	0.3050(9)	0.693(2)	5.9(6)
C17	0.4157(8)	0.3158(8)	0.589(1)	4.9(5)
C21	0.470(1)	0.4598(8)	0.317(2)	6.2(6)
C22	0.485(2)	0.5257(9)	0.289(4)	16(2)
C31	0.5535(9)	0.0574(8)	0.319(2)	6.6(7)
C32	0.533(1)	−0.008(1)	0.279(4)	12(1)
H1	0.5681(9)	0.0803(8)	0.394(2)	5*
H2	0.5877(9)	0.0536(8)	0.290(2)	5*
H3	0.540(1)	−0.002(1)	0.205(4)	5*
H4	0.7436(9)	0.365(1)	0.713(1)	5*
H4	0.559(1)	−0.041(1)	0.327(4)	5*
H5	0.8206(8)	0.265(1)	0.825(2)	5*
H5	0.507(1)	0.4722(8)	0.386(2)	5*
H6	0.7982(8)	0.181(1)	0.752(2)	5*
H6	0.449(1)	0.4957(8)	0.271(2)	5*
H7	0.7039(7)	0.1586(8)	0.578(1)	5*
H7	0.457(2)	0.5593(9)	0.247(4)	5*
H8	0.513(2)	0.5390(9)	0.370(4)	5*
H14	0.3878(9)	0.1604(8)	0.666(1)	5*
H15	0.3902(9)	0.2527(9)	0.800(1)	5*
H16	0.381(1)	0.3352(9)	0.729(2)	5*
H17	0.4181(8)	0.3594(8)	0.578(1)	5*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as:(4/3)-$[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

viz. $Li_2[Cr(Etbarb)_4] \cdot 2EtOH \cdot 0.5EtOH \cdot 0.5H_2O$, with $Z=8$. The atomic coordinates for this structure are listed in Table 3.

Selected bond distances and angles for the two structures are given in Tables 4 and 5.

Results and discussion

$Cr_2Sac_4 \cdot 2THF$

The structure of compound **1** is depicted in Fig. 1. There is a two-fold axis along the metal-to-metal bond. The saccharinate anions bridge the dichromium unit using their amidato portion. On any metal atom,

TABLE 3. Positional parameters and equivalent isotropic displacement parameters and their e.s.d.s for non-hydrogen atoms for $Li_2[Cr(Etbarb)_4] \cdot 2EtOH \cdot 0.5EtOH \cdot 0.5H_2O$ (**2**)

Atom	*x*	*y*	*z*	*B* (Å^2)[b]
Cr(1)	0.250	0.250	0.000	2.09(2)
N(1)	0.1937(2)	0.2560(3)	0.0698(2)	2.49(9)
C(1)	0.1809(2)	0.1828(3)	0.0867(3)	2.7(1)
C(2)	0.1388(3)	0.1666(4)	0.1344(4)	4.2(2)
C(3)	0.1165(2)	0.2392(4)	0.1615(3)	3.6(1)
N(2)	0.1321(2)	0.3074(3)	0.1379(3)	3.3(1)
C(4)	0.1684(2)	0.3197(3)	0.0923(3)	2.8(1)
O(1)	0.2024(2)	0.1270(2)	0.0627(2)	3.66(9)
C(5)	0.1601(4)	0.1176(5)	0.1902(5)	6.9(3)
C(6)	0.1975(5)	0.1555(9)	0.2274(5)	9.0(3)
C(7)	0.0976(3)	0.1231(6)	0.0964(6)	8.0(3)
C(8)	0.0757(4)	0.1701(8)	0.0409(7)	9.1(3)
O(2)	0.0842(2)	0.2371(3)	0.2036(3)	4.8(1)
O(3)	0.1762(2)	0.3852(2)	0.0743(2)	3.42(9)
N(3)	0.2040(2)	0.3007(3)	−0.0707(2)	2.40(9)
C(9)	0.2042(2)	0.3750(3)	−0.0916(3)	2.7(1)
C(10)	0.1700(2)	0.4018(3)	−0.1459(3)	3.1(1)
C(11)	0.1368(2)	0.3381(4)	−0.1711(3)	3.2(1)
N(4)	0.1393(2)	0.2679(3)	−0.1431(3)	3.2(1)
C(12)	0.1725(2)	0.2484(3)	−0.0946(3)	2.8(1)
O(4)	0.2315(2)	0.4245(2)	−0.0674(2)	3.64(9)
C(13)	0.1376(3)	0.4685(4)	−0.1219(4)	4.3(2)
C(14)	0.1036(3)	0.4463(5)	−0.0680(4)	5.8(2)
C(15)	0.2034(3)	0.4297(4)	−0.2019(3)	4.9(2)
C(16)	0.2397(3)	0.3699(6)	−0.2251(4)	6.3(2)
O(5)	0.1070(2)	0.3499(3)	−0.2146(2)	4.8(1)
O(6)	0.1727(2)	0.1816(2)	−0.0738(2)	3.8(1)
O(7)	−0.0045(2)	0.2138(3)	0.2892(3)	5.2(1)
C(17)	0.0100(4)	0.1845(8)	0.3482(6)	8.8(3)
C(18)	0.0603(5)	0.1535(7)	0.3484(6)	9.4(4)
Li(1)	0.0294(4)	0.3011(6)	0.2448(6)	4.4(2)
O, C(1S)[a]	0.233(1)	−0.290(2)	−0.061(1)	19.8(8)*
O(2S)	0.205(2)	−0.267(4)	−0.006(4)	19.8(8)*

[a] This site was modelled as 0.25 O + 0.25 C, as described in the text. [b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

TABLE 4. Selected bond distances (Å) and angles (°) and their e.s.d.s for $Cr_2(Sac)_4\cdot 2THF$ (**1**)

Distances (Å)	
Cr(1)–Cr(2)	2.550(4)
Cr(1)–O(1)	2.005(7)
Cr(1)–N(11)	2.087(12)
Cr(1)–O(31)	2.174(14)
Cr(2)–O(11)	1.988(10)
Cr(2)–N(1)	2.078(8)
Cr(2)–O(21)	2.183(14)
Angles (°)	
Cr(2)–Cr(1)–O(1)	89.7(3)
Cr(2)–Cr(1)–N(11)	82.4(3)
Cr(2)–Cr(1)–O(31)	180
O(1)–Cr(1)–N(11)	88.7(4)
O(1)–Cr(1)–O(1′)	179.4(4)
O(1)–Cr(1)–N(11′)	91.2(4)
Cr(1)–Cr(2)–O(21)	180
O(11)–Cr(2)–N(1)	89.2(4)
O(11)–Cr(2)–O(11′)	180.0(6)
O(1)–Cr(1)–O(31)	90.3(3)
O(11)–Cr(2)–N(1′)	90.8(4)
N(11)–Cr(1)–N(11′)	164.8(5)
N(11)–Cr(1)–O(31)	97.6(3)
Cr(1)–Cr(2)–N(1)	82.8(3)
Cr(1)–Cr(2)–O(11)	89.9(3)
O(11)–Cr(2)–O(21)	90.1(3)
N(1)–Cr(2)–N(1′)	165.7(4)
N(1)–Cr(2)–O(21)	97.2(3)

Numbers in parentheses are the e.s.d.s in the least significant digits.

the N and O atoms are in an alternating *cis*-oid arrangement. Each metal atom is also bound to a THF molecule located at the axial position.

One striking feature of the molecule is the very long chromium–chromium bond, namely 2.550(4) Å, which is the longest so far characterized for the dichromium species and the very short $Cr–L_{ax}$ distances, 2.174(14) and 2.183(14) Å, which represent the shortest $Cr–L_{ax}$ distances found on quadruply bonded chromium complexes*. Presumably both of these facts are interrelated and the long Cr–Cr bond is, at least partially, a consequence of the short $Cr–L_{ax}$ bond but an interesting question is why is the latter bond so short. A stick and ball model of the molecule shows that the cavity for the axial ligand is relatively small and probably for that reason the THF molecule is forced very close to the metal atom, which in turn elongates the metal-to-metal bond. The presence of N–Cr–N angles of *c.* 165° points in this direction. In most other dichromium compounds structurally characterized, the bond angles that are formed by the *trans* atoms and the metal atom are in the order of 170–180°. The distortion observed in this angle is probably due to the repulsion of the THF molecule and both of the sulfonyl groups. It is worthwhile to note that the O–Cr–O bond angles are not so important sterically and both are *c.* 180°.

TABLE 5. Selected distances (Å) and angles (°) and their e.s.d.s for $Li_2[Cr(Etbarb)_4]\cdot 2EtOH\cdot 0.5EtOH\cdot 0.5H_2O$ (**2**)

Distances	
Cr(1)–N(1)	2.105(4)
Cr(1)–N(3)	2.113(4)
N(1)–C(1)	1.349(7)
N(1)–C(4)	1.371(7)
N(3)–C(9)	1.345(7)
N(3)–C(12)	1.332(7)
Li(1)...O(1′)	1.98(1)
Li(1)...O(2)	2.03(1)
Li(1)...O(4′)	1.88(1)
Li(1)...O(7)	1.98(1)
Angles	
N(1)–Cr(1)–N(1′)	92.9(2)
N(1)–Cr(1)–N(3)	91.9(2)
N(1)–Cr(1)–N(3′)	157.7(2)
N(3)–Cr(1)–N(3′)	91.8(2)
Cr(1)–N(1)–C(1)	108.7(4)
Cr(1)–N(1)–C(4)	129.4(4)
C(1)–N(1)–C(4)	121.7(5)
Cr(1)–N(3)–C(9)	127.7(4)
Cr(1)–N(3)–C(12)	110.9(3)
C(9)–N(3)–C(12)	121.4(5)
O(1′)...Li(1)...O(2)	118.3(6)
O(1′)...Li(1)...O(4′)	121.0(6)
O(1′)...Li(1)...O(7)	106.2(6)
O(2)...Li(1)...O(4′)	109.5(7)
O(2)...Li(1)...O(7)	97.2(5)
O(4′)...Li(1)...O(7)	99.7(5)

Numbers in parentheses are e.s.d.s in the least significant digits.

Another factor that should be taken into account to explain the long Cr–Cr bond length is that the value of 4.7 for the pK_a of saccharine is relatively high, certainly much higher than the one for the related oxindole compound [4].

There is evidence from our laboratories that this compound is approaching the limiting distance between two chromium atoms in the tetrabridged complexes. When the THF molecules are substituted by pyridine, mononuclear and dinuclear complexes are isolated; and there is a well established equilibrium, in solution, between the two species [9].

$Li_2Cr(Etbarb)_4\cdot 2EtOH$

When $Cr_2OAc_4\cdot 2H_2O$ was reacted with LiEtbarb in stoichiometric amounts, in THF, Et_2O or EtOH, to try to obtain $Cr_2(Etbarb)_4$, we failed to isolate the compound. However, when the amounts of LiEtbarb were increased a very clean reaction occurs

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*The longest Cr–Cr bond length previously reported was 2.541(1) Å in $Cr_2(O_2CCF_3)_4\cdot 2Et_2O$, and the shortest Cr–L distance was 2.210(6) Å in $Cr_2(O_2CH)_4$ [3].

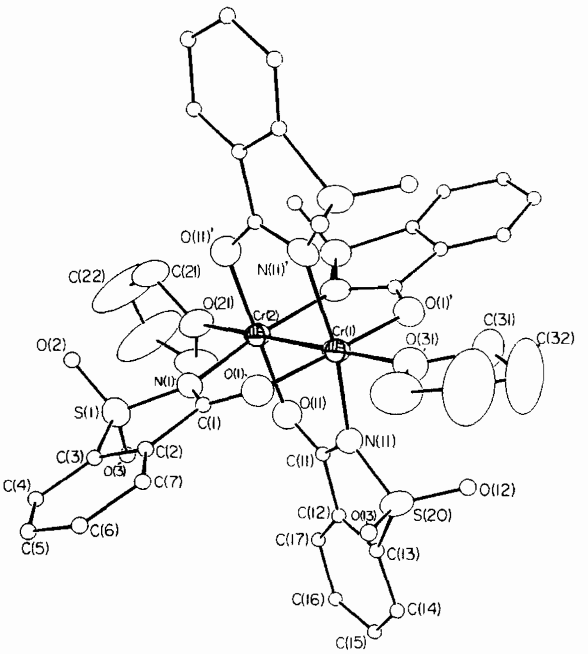

Fig. 1. ORTEP drawing of the molecular structure of $Cr_2Sac_4 \cdot 2THF$ (**1**). Peripheral atoms of the saccharinate ligands are rendered as small circles for clarity. All other sites are represented by their 40% probability ellipsoids.

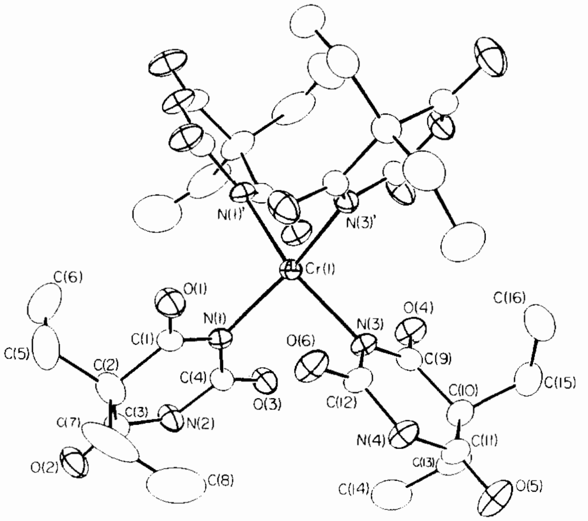

Fig. 2. ORTEP representation of the anion $[Cr(Etbarb)_4]^{2-}$ from **2**, showing the atom labelling scheme. All atoms are represented by their 40% probability ellipsoids.

and $Li_2Cr(Etbarb)_4 \cdot 2EtOH$ easily crystallized as a very air sensitive material.

Its structure is shown in Fig. 2. The metal-to-metal bond has been broken and the $Cr(Etbarb)_4{}^{2-}$ unit is four coordinate. The molecule has a crystallographic two-fold axis. The coordination about the chromium atom actually has S_4 symmetry. The rather flat tetrahedron could also be considered as a distorted square plane, in which the N(1)–Cr–N(3′) angle is 157.7(2)°.

The bonding structure of $Li_2[Cr(Etbarb)_4] \cdot 2EtOH$ is extended in three dimensions. Each lithium ion is coordinated in a distorted tetrahedral arrangement by four oxygen atoms — three of them from two different $[Cr(Etbarb)_4]^{2-}$ ions, and one from an ethanol molecule.

The reaction of Cr_2OAc_4 to produce mononuclear compounds is not new [3, 10], however, in most of the cases known, the reactions are with chelating or simple monodentate ligands. This is the first example of dichromium bond rupture from reaction with a ligand with the -N–C–O unit, which is normally considered a good bridging group for metal–metal bonded species.

Most other four-coordinated chromium(II) complexes structurally characterized are formed from chelating ligands, examples of which are the β-ketoamines [11], 1,2-dithiolato [12], polypyrazolylborato [10a], porphinato [13] although several non-chelating examples are known with ligands such as isothiocyanato [14] or bromides [15]. In almost all of these compounds the stereochemistry about the chromium atom is essentially planar, although there is at least one report of a complex with a pseudotetrahedral structure, namely $Cr(NO)[N(SiMe_3)]_3$. In the latter compound, the oxidation state of chromium is considered as II if the nitrosyl group is taken as NO^+ [16].

The presence of the square planar complexes of chromium(II) is normally taken as a manifestation of the Jahn-Teller effect for this d^4 system [1]. In the title compound, the additional distortion shown is probably due to the presence of the four sterically demanding diethylbarbiturate anions. Alternatively the complex can be viewed as the result of a Jahn-Teller compression of a tetrahedral pro-molecule. Either way, no electronic degeneracy remains in the distorted complex.

Supplementary material

Full listing of bond distances and bond angles (2 pages), anisotropic displacement parameters (2 pages) and observed and calculated structure factors (10 pages) for **1** as well as hydrogen atom coordinates (1 page), bond distances and bond angles (3 pages), anisotropic displacement parameters (2 pages) and observed and calculated structure factors (10 pages) for **2** are available on request from author F.A.C.

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References

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley, New York, 5th edn., 1988, Ch. 18, pp. 683–686.

2 (a) F. A. Cotton, G. E. Lewis, C. A. Murillo, W. Schwotzer and G. Valle, *Inorg. Chem., 23* (1984) 4038; (b) F. A. Cotton, L. R. Falvello, R. Llusar, E. Libby, C. A. Murillo and W. Schwotzer, *Inorg. Chem., 25* (1986) 3423; (c) F. A. Cotton, E. Libby, C. A. Murillo and G. Valle, *Inorg. Synth., 27* (1990) 306; (d) F. A. Cotton, L. R. Falvello, C. A. Murillo and G. Vallee, *Z. Anorg. Allg. Chem., 540/541* (1986) 67.

3 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms,* Wiley, New York, 1982, Ch. 4.

4 F. A. Cotton and W. Wang, *Polyhedron, 4* (1985) 1735.

5 R. A. Kok and M. B. Hall, *J. Am. Chem. Soc., 105* (1983) 676.

6 M. Ardon, A. Bino, S. Cohen and T. Felthouse, *Inorg. Chem., 23* (1984) 3450.

7 F. A. Cotton, M. W. Extine and G. W. Rice, *Inorg. Chem., 17* (1978) 176.

8 (a) F. A. Cotton, B. A. Frenz, G. Deganello and A. Shaver, *J. Organomet. Chem., 50* (1973) 227; (b) A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 18* (1979) 3558.

9 N. M. Alfaro, F. A. Cotton, L. M. Daniels and C. A. Murillo, unpublished results.

10 (a) F. A. Cotton and G. N. Mott, *Inorg. Chem., 22* (1983) 1135; (b) D. H. Gerlach and R. H. Holm, *Inorg. Chem., 8* (1969) 2292.

11 L. F. Larkworthy, D. H. Povey and B. Sandell, *Inorg. Chim. Acta, 83* (1984) L29, and refs. therein.

12 J. R. Dorfman, Ch. P. Rao and R. H. Holm, *Inorg. Chem., 24* (1985) 453.

13 W. R. Scheidt and C. A. Reed, *Inorg. Chem., 17* (1978) 710.

14 J. Jubb, L. F. Larkworthy, G. A. Leonard, D. A. Povey and J. Tucker, *J. Chem. Soc., Dalton Trans.,* (1989) 1631.

15 M. F. C. Ladd, L. F. Larkworthy, G. A. Leonard, D. C. Povey and S. S. Tandon, *J. Chem. Soc., Dalton Trans.,* (1984) 2351.

16 D. C. Bradley, M. B. Hursthouse, C. W. Newing and A. J. Welch, *J. Chem. Soc., Chem. Commun.,* (1972) 567.

Note added in proof

While this paper was in press a report appeared describing Cr_2(7-azaindolyl)$_4$(DMF)$_2$ which has a Cr–Cr distance of 2.604(2) Å. See J. H. Edema, S. Gambarotta, A. Meetsma, F. van Bolhuis, A. L. Spek and W. J. J. Smeets, *Inorg. Chem., 29* (1990) 2147.